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Abstract. The effect of quenching on the electrical resistivity and optical properties of $MoTe_2$ compound was studied. Significant changes were detected in the behaviour and value of the electrical resistivity, indicating an increase in the metallic (conductive) properties of the compound, which is in good agreement with the data of optical measurements.

1. Introduction

Topological materials – topological insulators (TIs) and topological semimetals (TSMs) – have been discovered relatively recently [1-8]. In TIs, their volume is a dielectric, and the surface behaves like a topologically protected metal with a linear dispersion law. In TSMs, the valence and conduction bands can be in contact at discrete points, which are also topologically protected. One type of TSMs is topological Weyl semimetals (TWSs). Quasiparticles in TWSs are “massless” Weyl fermions, which are chiral particles with zero effective mass and a linear dispersion law near the Weyl points. Gapless surface states – Fermi arcs – connect the projections of the Weyl points of opposite chirality onto the surface Brillouin zone. Current carriers in the “near-surface” layer of TIs and TWSs are spin-polarized, that can find application in spintronics, and the presence of “massless” charge carriers in TWSs can be used in ultrafast micro- and nanoelectronic devices.

There is a large class of materials called transition metal dichalcogenides (TMDs), some of which are TWSs. TMDs are a large group of compounds with the chemical formula MX_2, where M is a transition metal and X is a chalcogen. It is known that $MoTe_2$ compound belongs to the TMD group and can exhibit the TWS properties. At the same time, the crystal structure of $MoTe_2$ and its electronic characteristics, in particular, electrical resistivity, strongly depend on the heat treatment. So, in “ordinary” synthesis of $MoTe_2$ compound, it exhibits semiconductor characteristics: high values of electrical resistivity and the "semiconductor" type of its temperature dependence $\rho(T)$. Quenching leads to the fact that the value of electrical resistivity decreases significantly, and $\rho(T)$ becomes “metallic”, increasing with temperature [9, 10]. Apparently, similar changes should be observed in the behaviour of other electronic properties of $MoTe_2$ compound, in particular, in its optical properties. Therefore, the aim of this work is to study the effect of quenching on the electrical resistivity and optical characteristics of $MoTe_2$.

2. Experimental

$MoTe_2$ single crystals were prepared by the chemical vapor transport method using Br_2 as a transport agent. Molybdenum and tellurium powders in a stoichiometric ratio were placed in a quartz ampoule with a length of 24 cm and a diameter of 1.5 cm. The ampoule was evacuated to a pressure of ~10^{-4} atm. The bromine vapor density was approximately 5 mg/cm^3. Then, the sealed quartz ampoule was placed in a horizontal tube furnace with a linear temperature gradient. The temperature of the hot zone was 850°C, crystal growth occurred in the cold zone at a temperature of 770°C. Single crystals were grown for 500 hours followed by slow cooling to room temperature. X-ray diffraction analysis revealed that $MoTe_2$ before quenching crystallizes in a hexagonal structure with the lattice parameters a = 3.540(7) Å and c = 13.983(5) Å. $MoTe_2$ compound is known to undergo a structural transition from hexagonal to monoclinic at a temperature of ~ 880°C [11]. Therefore, some single crystals were again placed in a quartz ampoule, which was also evacuated, heated to 910°C, maintained at this temperature for 1 hour, and quenched in water. The chemical composition of the samples was confirmed by X-ray microanalysis using a FEI Inspect F scanning electron microscope equipped with an EDAX attachment.

The temperature dependences of the electrical resistivity *ρ(T)* were measured by the standard method (see, e.g. [12, 13]) in the temperature range from 80 to 300 K. The optical constants, the refractive index n and the absorption coefficient k, were measured using the Beattie method with one reflection from the plane of the samples in the spectral range of 0.4-5.0 eV at room temperature. The measurement error was 2–4% in the visible and ultraviolet (VUV) regions and ~ 6% in the middle infrared (IR) region. The values of n and k were used to calculate the real $\varepsilon_1(\omega) = n^2 - k^2$ and imaginary $\varepsilon_2(\omega) = 2nk$ parts of the complex dielectric permittivity ε, the real part of the complex optical conductivity $\sigma(\omega) = nk\omega / 2\pi$ (ω is the cyclic frequency of the light wave) and reflectivity

$$R(\omega) = \frac{[(n-1)^2 + k^2]}{[(n+1)^2 + k^2]}.$$

3. Result and discussions

Figure 1 shows the temperature dependences of electrical resistivity *ρ(T)* of $MoTe_2$ before (a) and after (b) quenching in the temperature range from 80 to 300 K. The dependence *ρ(T)* of $MoTe_2$ before quenching (figure 1a) demonstrates a "semiconductor" behaviour at temperatures from 80 to 190 K, after which a relatively small increase in resistivity is observed. The resistivity value is ~ (550-850) mOhm·cm, which is typical for semiconductors.

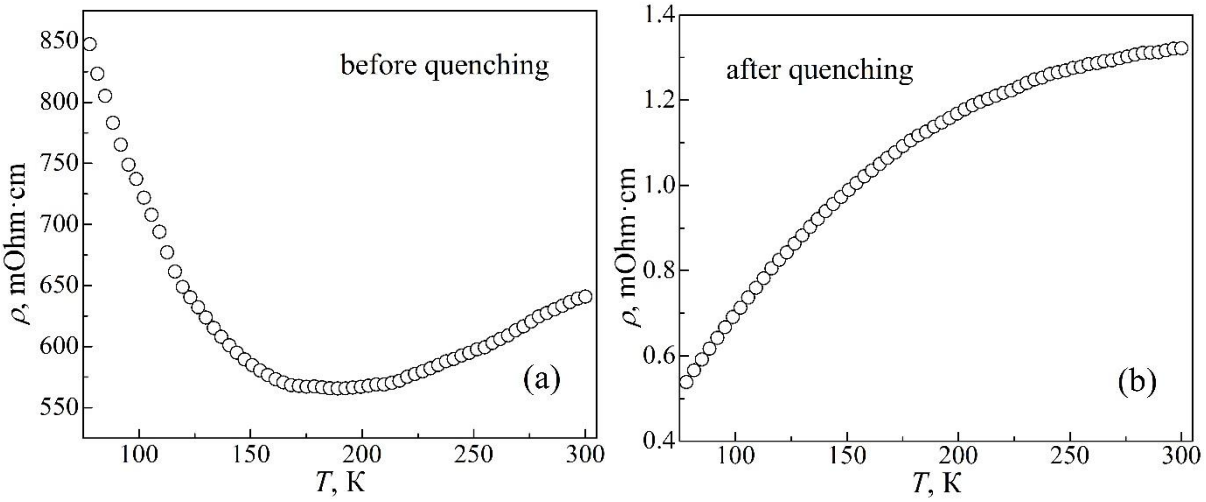

Figure 1. The temperature dependences of electrical resistivity of $MoTe_2$ before (a) and after (b) quenching.

As can be seen from figure 1b, quenching leads to a drastic change in the behaviour and value of electrical resistivity of $MoTe_2$. The temperature dependence of electrical resistivity $\rho(T)$ of $MoTe_2$ after quenching shows a "metallic" type with a resistivity value of ~ (0.3-1.3) mOhm·cm, which is approximately three orders of magnitude less than the resistivity of $MoTe_2$ before quenching. Apparently, similar changes should be observed in other electronic properties, in particular, in optical ones.

Optical studies of $MoTe_2$ in the initial state and after quenching are presented in figures 2-4. It is known that the main role in the formation of optical properties in metals and alloys in the infrared region of the spectrum is played by the mechanism of intraband acceleration of electrons by the light wave field [14]. Negative values of the real part of the complex dielectric permittivity in the infrared (IR) region of the spectrum are the optical criterion for the metallic type conductivity of a substance. In the visible and ultraviolet (VUV) ranges, the interband absorption, i.e. the quantum absorption of light with the transfer of electrons from lower energy states to free upper states, dominates, which gives information about the electron energy spectrum. The complex dielectric permittivity is the sum of the contributions from the intraband and interband absorption mechanisms that can coexist in a certain energy range. Positive values of the real part $\varepsilon_1(\omega)$ and numerous features (peaks, kinks) on the imaginary part $\varepsilon_2(\omega)$ of the dielectric permittivity curve (figure 2) indicate the predominance of the interband absorption mechanism in the entire studied range. In the IR range, we note the low values of $\varepsilon_2(\omega)$ and the positive values of $\varepsilon_1(\omega)$, which suggests that there is no contribution from free carriers up to the boundary of the studied range of 0.4 eV. Negative values ε_1 at $E > 2.4$ eV (VUV range) indicate a weakening of the interband absorption.

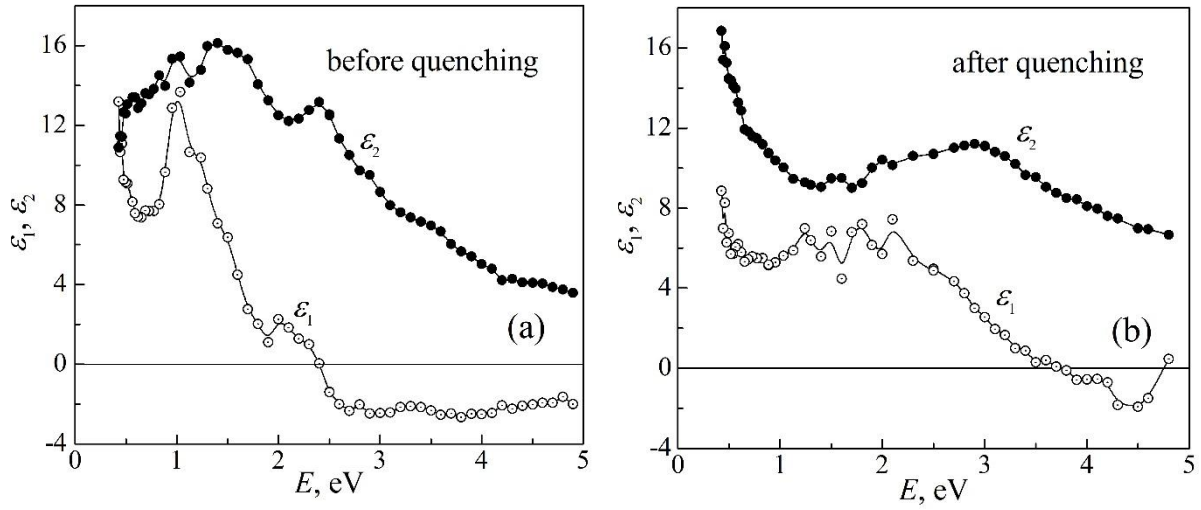

Figure 2. Dispersions of the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the complex dielectric permittivity of $MoTe_2$ before (a) and after quenching (b).

As a result of quenching, the dispersion of the dielectric permittivity has undergone significant changes. The shape of the curves, the ratio of intensities in different regions of the spectrum have changed. The values of $\varepsilon_1(\omega)$ remain positive already in a wider range of energies and become negative at an energy $E > 3.8$ eV. The main feature is the appearance of a rise in the imaginary part $\varepsilon_2(\omega)$ of the complex dielectric permittivity in the IR range. This indicates the appearance of a contribution of free carriers to optical absorption.

Figure 3 shows the reflectivity curves $R(\omega)$ of $MoTe_2$. The reflectivity has low values, varying from 0.39 to 0.48. A change in reflectivity dispersion as a result of heat treatment has been noted. The main feature is an increase in R at energies $E < 1.5$ eV, which also indicates the appearance of a contribution of free carriers to optical absorption.

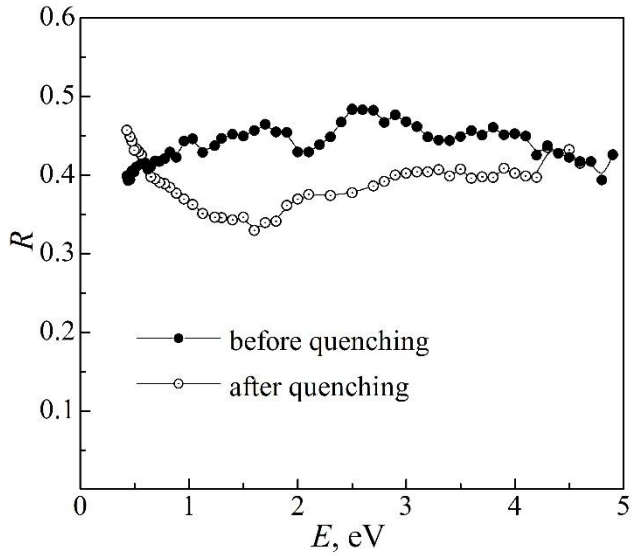

Figure 3. Dispersions of the reflectivity *R(ω)* of $MoTe_2$ before and after quenching.

Figure 4 shows the dispersion of the optical conductivity of $MoTe_2$ in the initial state and after quenching. The optical conductivity spectrum *σ(ω)* of the sample before quenching is a single wide band centered at 2.4 eV, formed by interband transitions. It is also possible to distinguish peaks at energies 1.7 eV and 3.5 eV. In the IR region of the spectrum, a sharp decrease in the optical conductivity is observed. It is known that, in the limit $\omega \to 0$, the optical conductivity approaches the static value $\sigma_0 = 1/\rho$. The value of the static conductivity at room temperature is marked on the ordinate axis ($E = 0$). Obviously, the curve *σ(ω)* tends to the value $\sigma_0 = 0.14 \cdot 10^{14}$ s^{-1}.

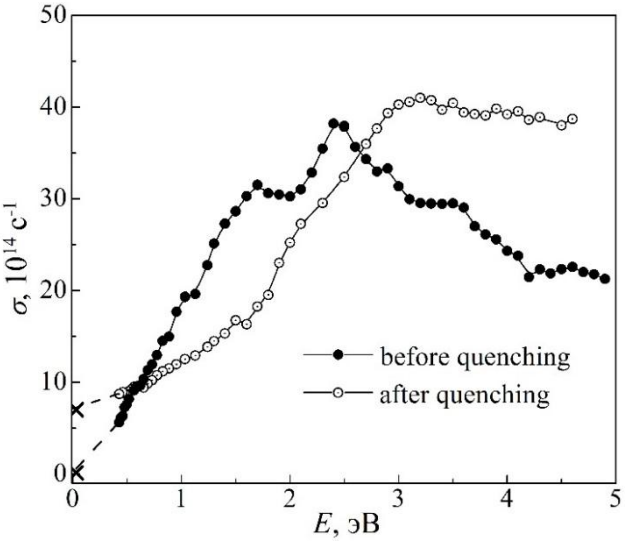

Figure 4. Dispersions of the real part of the complex optical conductivity *σ(ω)* of $MoTe_2$ before and after quenching. The symbols (x) on the ordinate axis *E = 0* show the values of the static conductivity at room temperature, obtained from measurements of electrical resistivity.

The optical spectrum of the quenched sample has undergone significant changes. The ratio of the optical conductivity intensities in different regions of the spectrum has changed. In the VUV range, the optical conductivity has become noticeably higher, and the edge of the absorption band has shifted toward higher energies by about 0.7 eV. In the limit $\omega \to 0$, the optical conductivity *σ(ω)* approaches $\sigma_0 = 7 \cdot 10^{14}$ s^{-1}. Changes in the spectral dependence of the optical conductivity indicate changes in the electronic energy spectrum as a result of quenching.

4. Conclusions

$MoTe_2$ single crystals in hexagonal modification were grown; some of which were quenched. The effect of quenching on the electrical resistivity and optical properties of the $MoTe_2$ was investigated.

The studies show significant changes in the electronic properties of $MoTe_2$ before and after quenching: the temperature dependence of the electrical resistivity changes from “semiconductor” to “metallic”, while the value of electrical resistivity decreases by about three orders of magnitude. These data are in good agreement with optical measurements, which also indicate an improvement in the metallic (conductive) properties of $MoTe_2$ after quenching.

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References
[1] Zhang H, Liu C-X, Qi X-L, Dai X, Fang Z and Zhang S-C 2009 *Nat. Phys.* **5** 438
[2] Xu S-Y et al. 2015 *Science* **349** 613
[3] Wu Y, Mou D, Jo N H, Sun K, Huang L, Bud'ko S L, Canfield P C and Kaminski A 2016 *Phys. Rev. B* **94** 121113
[4] Liu Y H, Chong C W, Jheng J L, Huang S Y, Huang J C A, Li Z, Qiu H, Huang S M and Marchenkov V V 2015 *Appl. Phys. Lett.* **107** 12106
[5] Liu Y, Chong C, Chen W, Huang J A, Cheng C, Tsuei K, Li Z, Qiu Hi and Marchenkov V V 2017 *Japanese Journ. of Appl. Phys.* **56** 70311
[6] Marchenkov V V, Domozhirova A N, Makhnev A A, Shreder E I, Naumov S V, Chistyakov V V, Huang J C A and Eisterer M 2019 *Low Temp. Phys.* **45** 241
[7] Marchenkov V V, Domozhirova A N, Makhnev A A, Shreder E I, Lukoyanov A V, Naumov S V, Chistyakov V V, Marchenkova E B, Huang J C A and Eisterer M 2019 *JETP* **128**(6) 939
[8] Marchenkov V V et al. 2019 *Journal of Physics: Conf. Series* **1199** 012037
[9] Lv Y-Y et al. 2017 *Sci. Rep.* **7** 44587
[10] Keum D H et al. 2015 *Nat. Phys.* **11** 482
[11] Vellinga M B, de Jonge R and Haas C 1970 *J. Solid State Chemistry* **2** 299
[12] Volkenshtein N V, Glin’ski M, Marchenkov V V, Startsev V E and Cherepanov A N 1989 *Sov. Phys. JETP* **95** 2103
[13] Cherepanov A N, Marchenkov V V, Startsev V E, Volkenshtein N V and Glinskii M 1990 *J. Low Temp. Phys.* **80** 135
[14] Sokolov A V 1961 *Optical Properties of Metals, in Russian* (Moscow: GIFML)